

The Effect of Chlorides on the Correlation of Accelerated Laboratory Corrosion Tests to Out-Door Exposure Tests for Ceramics-Aluminum Couples

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Presentation Outline

- Introduction
- Objectives
- Materials
- Procedures
- Background
- Results and Discussion
- Conclusion



Introduction

- Today, many components and equipment are comprised of a material system rather than a single type of material.
 - For example, today's automobiles use on the order of 100 kg of polymers compared to only 3 kg in the 1980s [1].
- To reduce weight and increase performance, more and more advanced systems and machines are being developed using alloys, composites, polymers, and ceramics.
 - A system of dissimilar materials, however, is a potential corrosion problem.
 - Metal alloys coupled to ceramics may lead to crevice and galvanic corrosion problems.
- Hence, in order to take advantage of material systems, compatibility issues must be thoroughly understood.
- The major focus of this study was the corrosion behavior of 6061-T6 Al coupled to various bulk ceramics exposed in the laboratory and natural environments.

Objectives

- Correlate the outdoor exposure corrosion-rate data from a variety of microclimates to a series of accelerated laboratory corrosion tests
 - Both galvanic and non-galvanic aluminum–ceramics couples were studied
 - 6061-T6 Al coupled to TiB_2 , B_4C , SiC , AlN , or Si_3N_4 .
- Modify accelerated corrosion test to better simulate corrosion behavior in the field.
 - Electrolytes with varying amounts of chlorides (i.e., 0, 10, 100, 1,000, 6,000 and 20,000 ppm chlorides) were used in the accelerated tests.
 - Duration of the accelerated corrosion tests was adjusted to better represent the corrosion damage accumulated in the field.
- Identify the governing corrosion mechanism using polarization experiments.

Materials

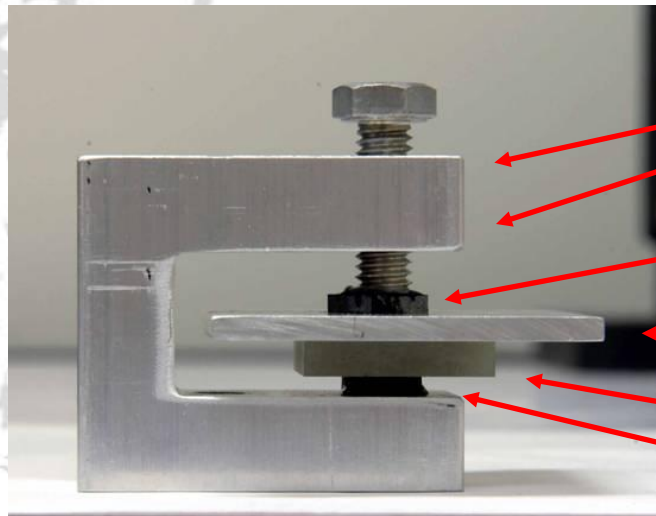
- The selection of the ceramic specimens was based primarily on their electrical resistivity.
 - Low electrical resistivity can increase the galvanic effect between the ceramic and the adjacent metal.
- The ceramics used in this research were manufactured by Ceradyne, Inc., CA.

Ceramic Properties [1]

Materials	Electrical resistivity (Ohm-cm)	Density (g/cm ³)	Thermal expansion coeff. 10 ⁻⁶ /°C; (RT – 1000°C)	Thermal conductivity (W/mK)@ 25°C
TiB ₂	10 ⁻⁵	4.5	8.2	25
B ₄ C	10 ¹	2.5	5.6	90
SiC	10 ⁷	3.2	4.8	115
Si ₃ N ₄	10 ¹⁴	3.1	3.2	42
AlN	10 ¹⁵	3.26	4.9	180-200

Procedures

- Ceramics were coupled to 6061-T6 Al using an insulated holder.



6061-T6 Al

Insulator
(G-10 fiber glass)

6061-T6 Al Coupon

Ceramic Coupon

Insulator (G-10 fiber glass)

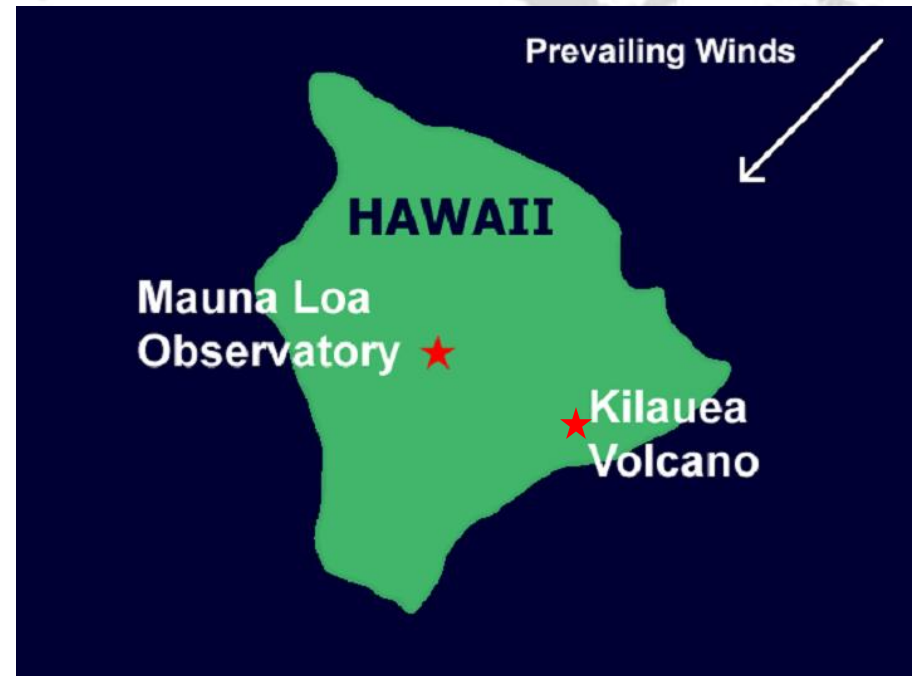
The interface pressure between
the aluminum and ceramic
coupons was approximately 2000
psi.

- Assembled couples were exposed in the field or in the laboratory

Procedures

Outdoor Exposure

- Field specimens were exposed for 3 months at eight different test sites (i.e., rain forest, alpine, marine (2 locations), volcanic, industrial, agricultural, and arid).
- Hawaii's climate is one of the most spatially diverse on Earth.



Procedures

Outdoor Exposure

Coconut Island*



- Marine environment

Kahuku*

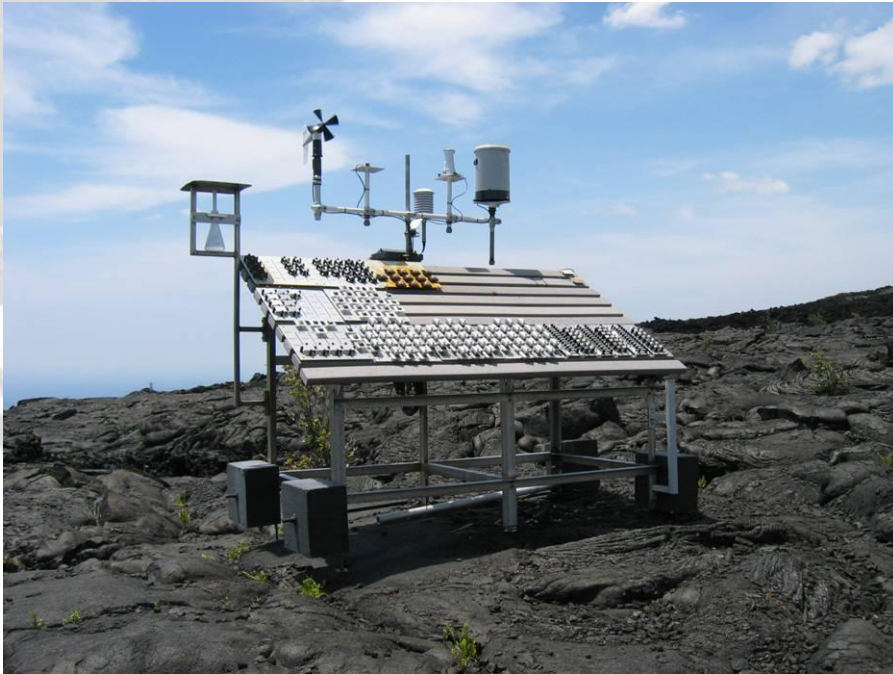


- Marine environment

Procedures

Outdoor Exposure

Kilauea Volcano*



- Volcanic and marine environment
- Acid rain: pH 3 - 4
- Variable humidity
- Sulfur dioxide plume

Campbell Industrial Park*



- Industrial environment
- Low humidity and rainfall
- Presence of sulfur
- Moderate chloride ion concentrations

Procedures

Outdoor Exposure

Waipahu*



- Dry climate
- Low humidity and rainfall
- Low time of wetness
- Low chloride ion concentrations

Ewa Nui*



- Agricultural environment
- Low humidity and rainfall
- Low time of wetness
- Low chloride ion concentrations

Procedures

Outdoor Exposure

Manoa*



- Rainforest climate
- High rainfall
- High humidity and time of wetness
- Low chloride ion concentrations

Mauna Loa Observatory*



- Alpine environment (11,000 feet elevation.)
- Low humidity and rainfall
- Low time of wetness
- Low chloride ion concentrations
- High solar radiation exposure

Procedures

Controlled Exposure

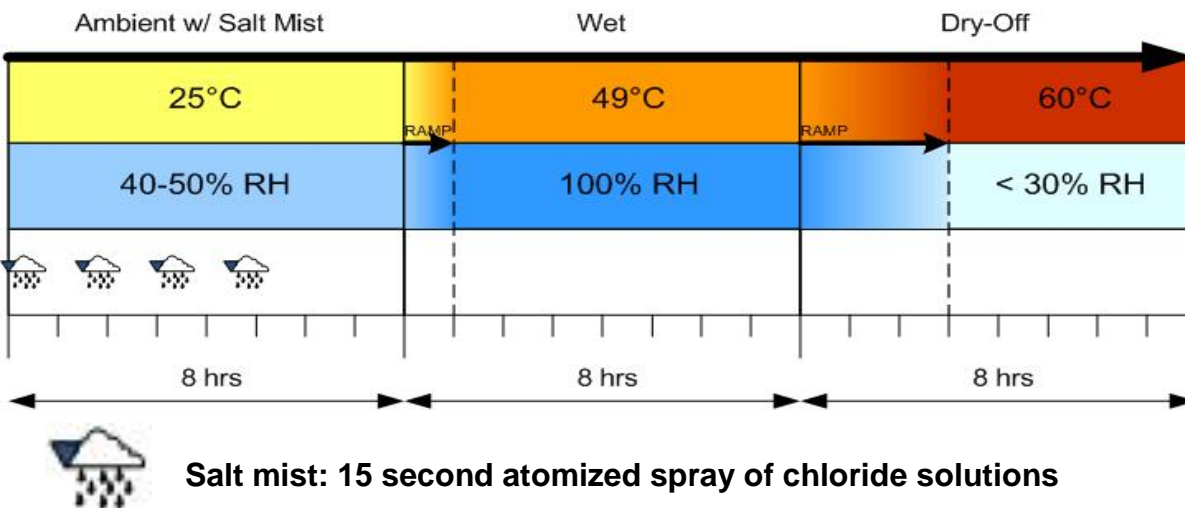
- Humidity-chamber experiments
 - The 6061-T6 Al–ceramic couples were dipped in electrolytes for 1 minute prior to placing inside the humidity chamber
 - simulated fresh water - 0.5 M sodium sulfate (Na_2SO_4)
 - simulated seawater - 3.15 wt% sodium chloride (NaCl), ASTM seawater, and real seawater
 - The chamber was maintained at 90% relative humidity (RH) and 30°C, and experiments were conducted for 90 and 21 days.



Procedures

Controlled Exposure

- Cyclic corrosion test chamber (CCTC) - Singleton
 - Modified GM9540P standard: The couples were exposed at **30° to the horizontal** (similar to outdoor exposure)
 - GM9540P solution: 0.9% sodium chloride, 0.1% calcium chloride, 0.25% sodium bicarbonate (6000 ppm Cl⁻)
 - Various chloride concentrations in 0.5 M Na₂SO₄
 - 0, 10, 100, 1000 ppm Cl⁻
 - Experiments were conducted for 2 and 24 cycles (24-hour).



CCTC Setup

A faint, light gray world map serves as the background for the slide, showing the outlines of continents and major landmasses.

Procedures

Electrochemical

- Polarization experiments
 - Electrodes were stabilized at the open-circuit potential for 1 hour before scanning at a rate of 1 mV/sec at 30°C.
 - De-aerated 0.5 M Na_2SO_4 solutions with various additions of NaCl.
 - 0, 10, 100, 1,000, 10,000 ppm Cl^- .
 - De-aerated 3.15 wt% NaCl ($\approx 20,000$ ppm Cl^-)

Procedures

Cleaning

- Corroded 6061-T6 Al coupons were cleaned according to International Standard ISO 8407: 1991 (E) C.1.1. (2% chromium tri-oxide and 5% phosphoric acid solution).

Calculation of Corrosion Rates

- Corrosion rates of 6061-T6 Al given in grams per meter squared per day (gmd) were calculated at the interface region using the following equation:

$$\text{Corrosion rate at the interface region} = \frac{\left[\text{mass loss of 6061-T6 Al in the couple} \right] - \left[\text{estimated mass loss of 6061-T6 Al outside the interface region} \right]^*}{\text{area of interface} \times \text{exposure time}}$$

$$\begin{aligned} * \text{ estimated mass loss of 6061-T6 Al outside the interface region} &= \text{mass loss of uncoupled 6061-T6 Al in the same environment} \times \text{Area fraction outside of the interface region (=8/9)} \end{aligned}$$

Background

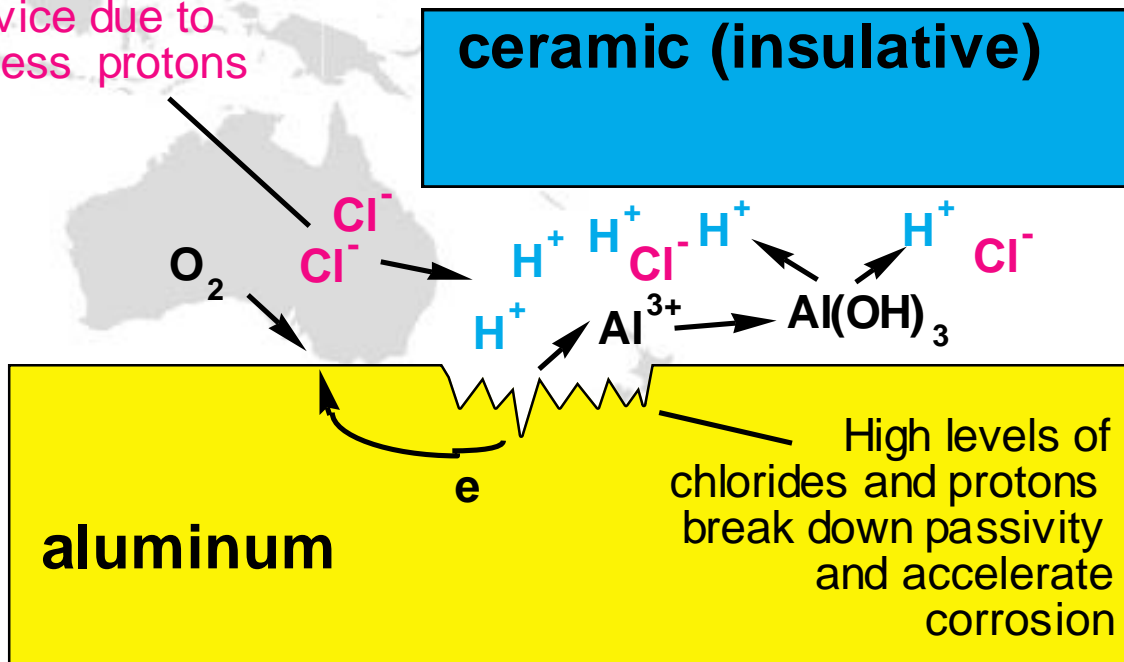
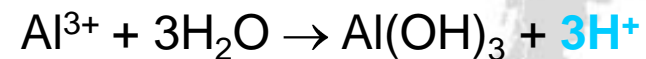
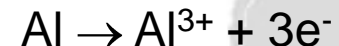
Crevice Corrosion

- If the ceramics are insulators, accelerated corrosion at the interface is governed primarily by crevice corrosion.

Chlorides migrate into crevice due to excess protons

ceramic (insulative)

Formation of aluminum hydroxide or alumina makes the crevice more acidic:



aluminum

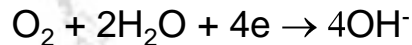
High levels of chlorides and protons break down passivity and accelerate corrosion

Background

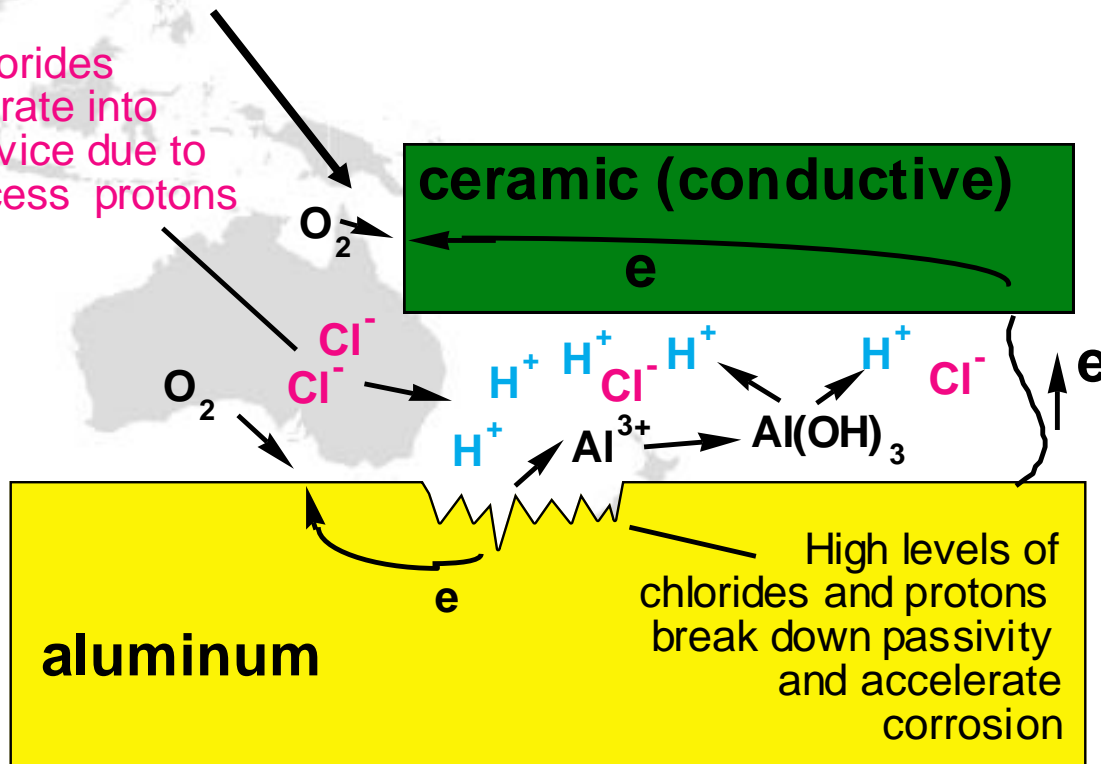
Crevice and Galvanic Corrosion

- If the ceramics are conductors, crevice corrosion at the interface can be accelerated by galvanic action:

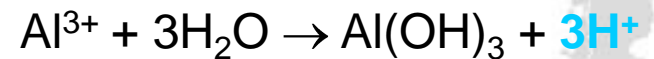
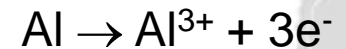
Oxygen reduction on the ceramic enhances crevice corrosion:



Chlorides migrate into crevice due to excess protons



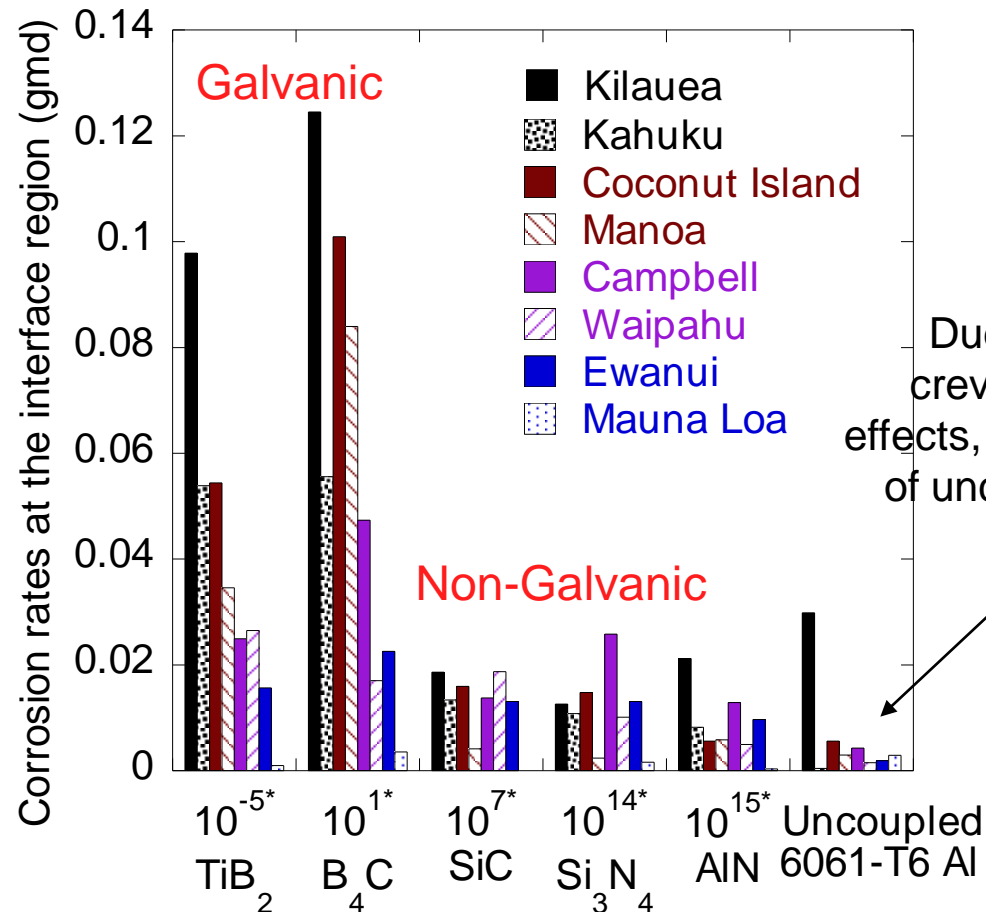
Formation of aluminum hydroxide or alumina makes the crevice more acidic:



Results and Discussion

Outdoor Exposure (3 Months)

Corrosion rates of the 6061-T6 Al coupons in the non-galvanic couples with SiC, AlN, or Si₃N₄ were generally lower than those of the galvanic couples with TiB₂ and B₄C.

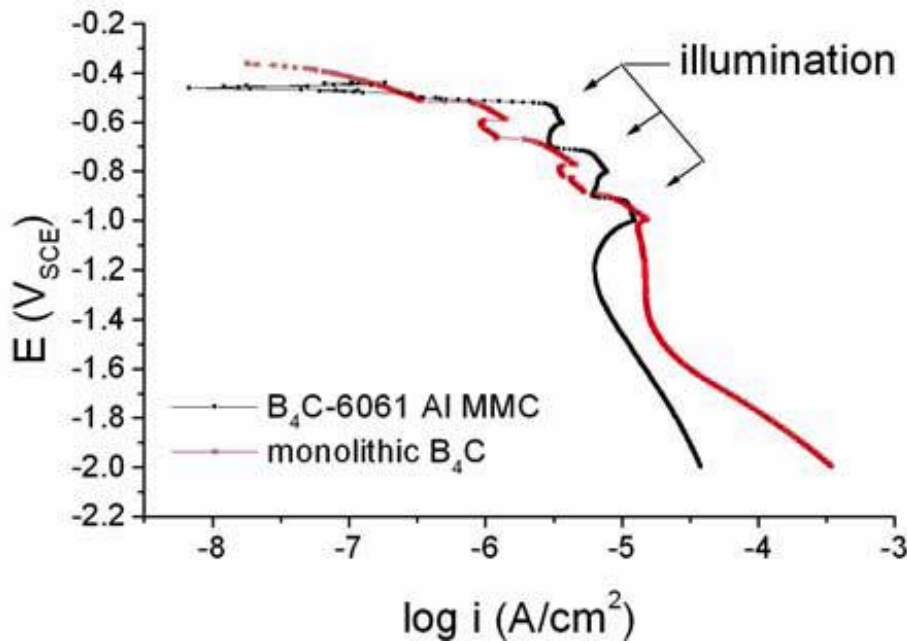


* Electrical resistivity of ceramics (Ω-cm)

Results and Discussion

Outdoor Exposure (3 Months)

- The highest corrosion rates were recorded when 6061-T6 Al coupons were coupled to the second most conductive B_4C ceramic, rather than the most conductive TiB_2 ceramic.
 - This could be caused by the photoelectrochemical properties of B_4C , which is a semi-conductor.

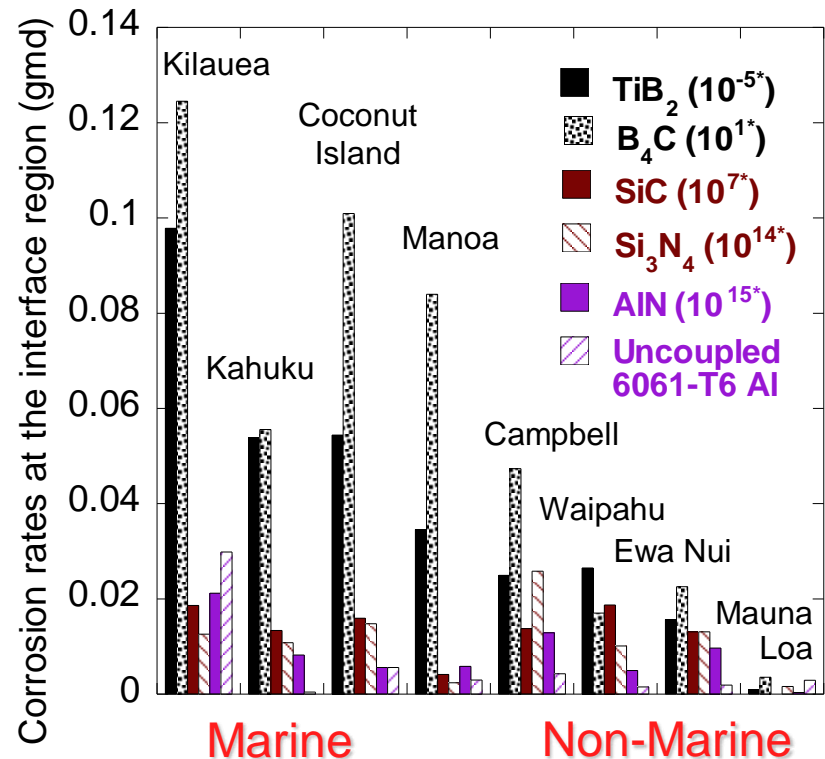


Hongbo Ding and L.H. Hihara, "Cathodic polarization diagrams of a monolithic B_4C electrode and an Al/ B_4C MMC in air-exposed 0.5 M Na_2SO_4 solution both in the dark and under illumination," ECS 214 Meeting.

Results and Discussion

Outdoor Exposure (3 Months)

- Effect of test site
 - The highest corrosion rate of 6061-T6 Al coupled to each type of ceramic occurred at Kilauea, possibly due to the high sulfur dioxide content in the air.
 - Rain pH levels can be as low as 3.
 - Corrosion rates were higher in marine environments (Kilauea, Coconut Island and Kahuku) due to high Cl^- deposition, and in the rainforest environment (Manoa) due to high wetness when compared to other test sites.



*Electrical resistivity of ceramics ($\Omega\text{-cm}$)

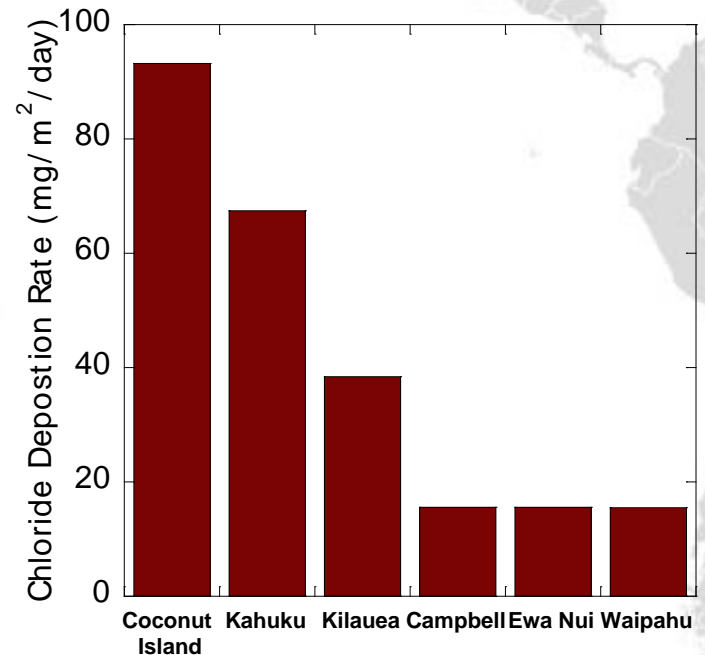
Results and Discussion

Outdoor Exposure (3 Months)

Weather Data*

Test Sites	Average Temperature (°F)	Average Humidity (%RH)	Rain (Inches)
Manoa	70.23	86.73	119.35
Coconut Island	73.90	79.27	25.56
Kilauea	65.04	81.7	24.25
Kahuku	78.62	71.46	4.3

Chloride Deposition Rate*

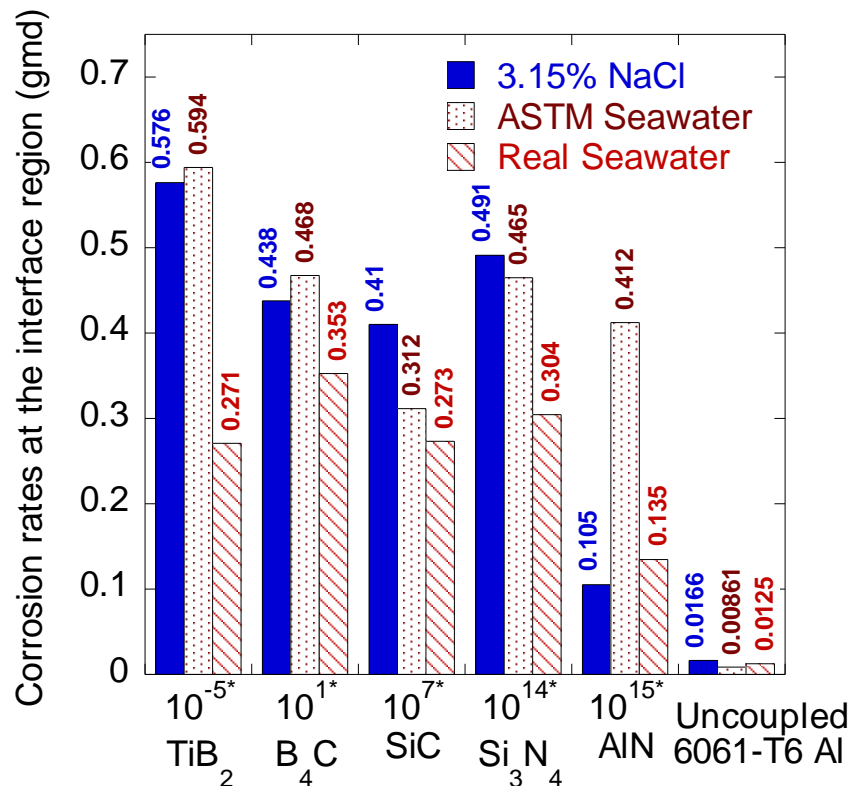


* From George Hawthorn of Hawaii Corrosion Lab

Below detection limit at Manoa and Mauna Loa

Results and Discussion

Humidity Chamber Exposure (90 Days) Chloride-Containing Electrolytes



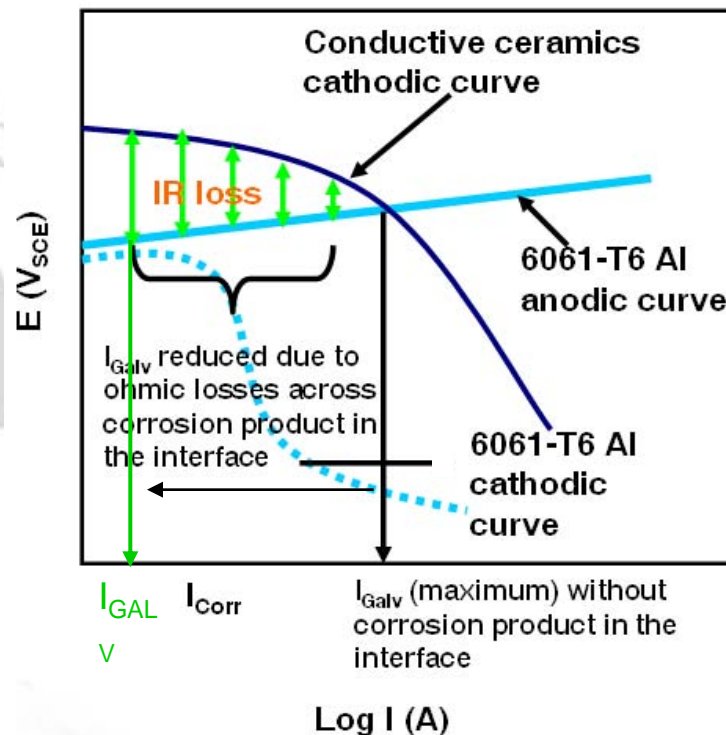
- The trend of high corrosion rates for the galvanic couples (as seen in the outdoor experiments) was not observed in the 90-day humidity chamber tests using chloride-containing solution treatments.
 - Corrosion rates for the galvanic and non-galvanic couples were high and comparable.
- One possible reason is that the chloride treatments were too aggressive and did not represent the conditions at the field sites.

*Electrical resistivity of ceramics (Ω-cm)

Results and Discussion

Humidity Chamber Exposure (90 Days)

- When corrosion at the ceramic-Al interface becomes substantial, the insulative aluminum oxide corrosion products could decouple the ceramic from the Al, attenuating galvanic effects.
- As a result, crevice corrosion can dominate, resulting in corrosion rates relatively independent of the ceramic resistivity.
 - Hence, galvanic and non-galvanic couples could subsequently corrode at comparable rates.

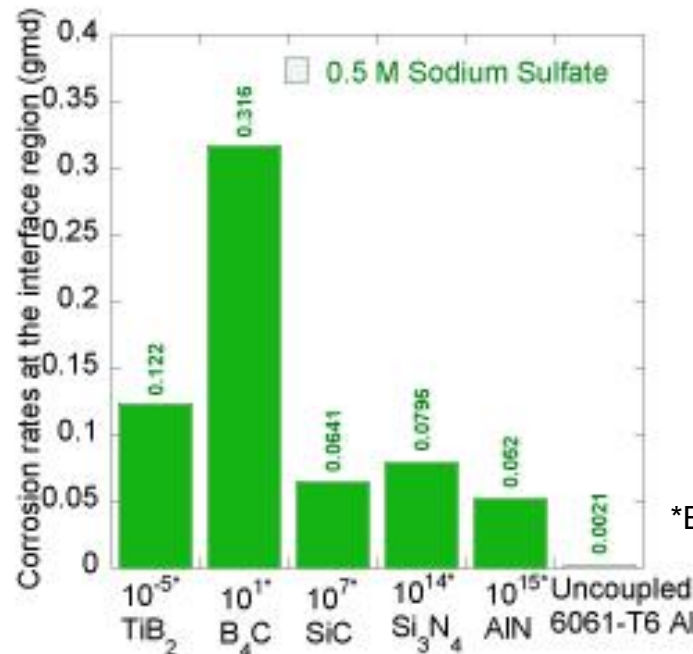


Results and Discussion

Humidity Chamber Exposure (90 Days)

Chloride-Free: 0.5 M Na₂SO₄ Treatment

- The coupons treated with 0.5 M Na₂SO₄ (less corrosive than Cl-containing electrolytes) showed similar trends to the field studies.



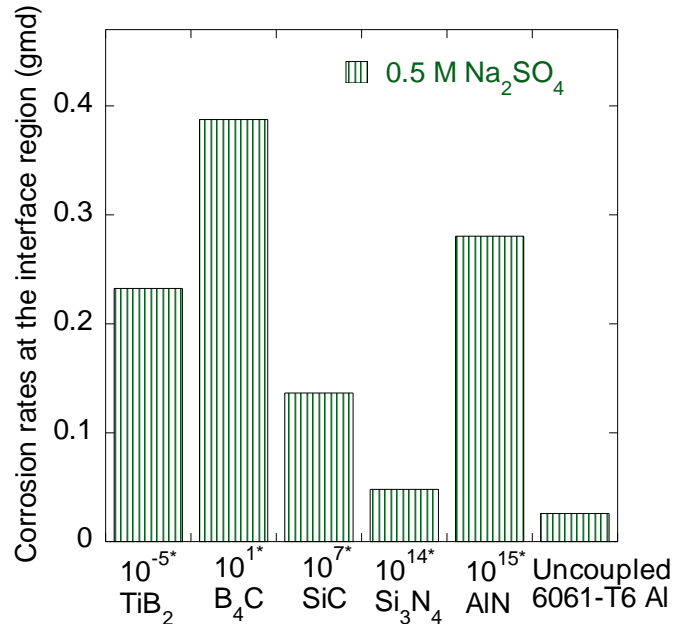
*Electrical resistivity of ceramics (Ω-cm)

- Lower amount of corrosion may have prevented galvanic decoupling in the interface.
- To test this hypothesis, humidity chamber experiments were conducted for a much shorter period (i.e., 21 days) to limit corrosion at the interface.

Results and Discussion

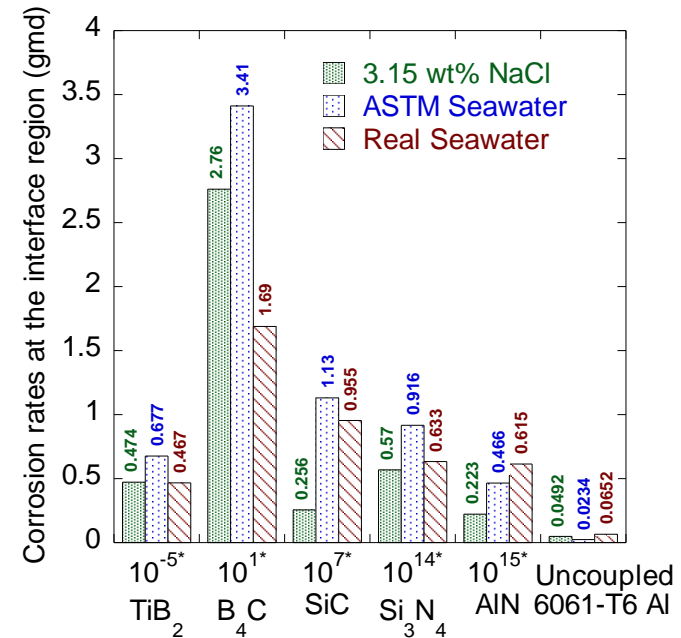
Humidity Chamber Exposure (21 Days)

Sulfate-exposure



Chloride-exposure

Corrosion rates at the interface region (HC21)



- Sulfate-exposure
 - Corrosion rates showed some similar trends to the outdoor tests.
- Chloride-exposure
 - Correlation improved, but corrosion rate of 6061-T6 Al was lower when coupled to conductive TiB₂ compared to many of the insulative ceramics.

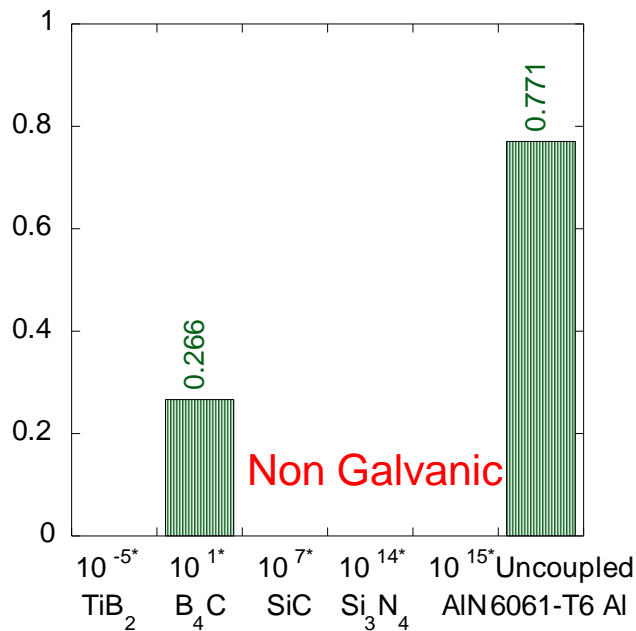
*Electrical resistivity of ceramics ($\Omega\text{-cm}$)

Results and Discussion

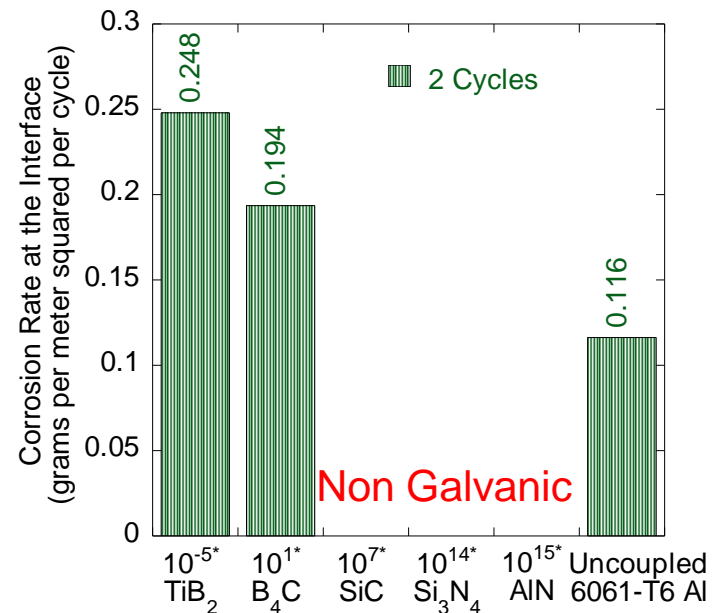
CCTC Experiment (2 cycles)

- Two cycles of the GM 9540
 - Equivalent to ≈ 400 days of 6061-T6 Al field exposure in moderate marine atmospheres based on mass loss of bare coupons.[#]

GM9540P Solution[#] Treatment



0.5 M Na₂SO₄ Solution Treatment



GM9540P solution: 0.9% sodium chloride, 0.1% calcium chloride, 0.25% sodium bicarbonate (6000 ppm Cl⁻)

*Electrical resistivity of ceramics ($\Omega\text{-cm}$)

[#] Sugamoto, Hawthorn, Hihara, ACS, 2008.

Results and Discussion

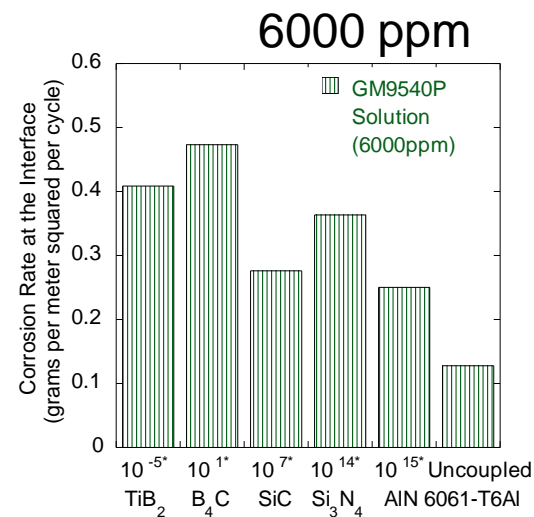
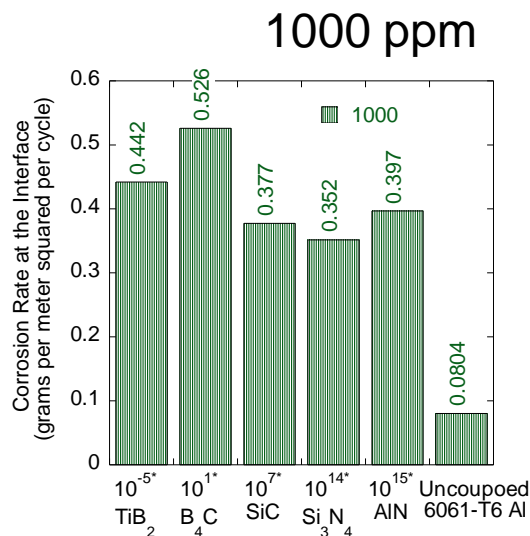
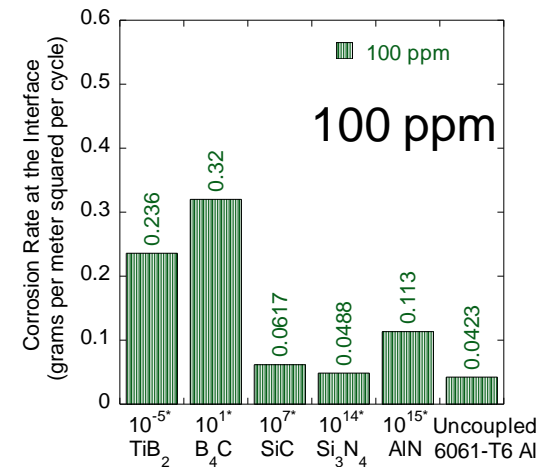
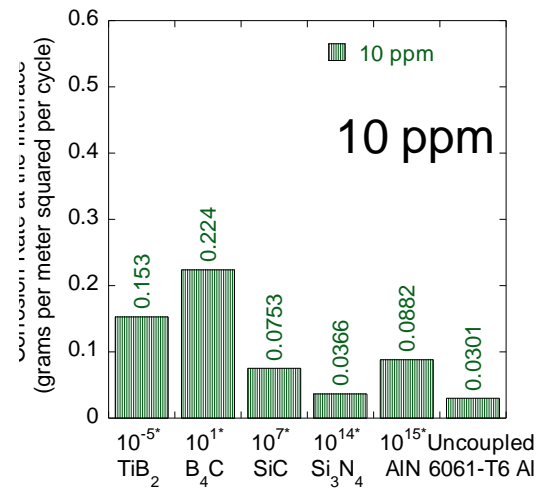
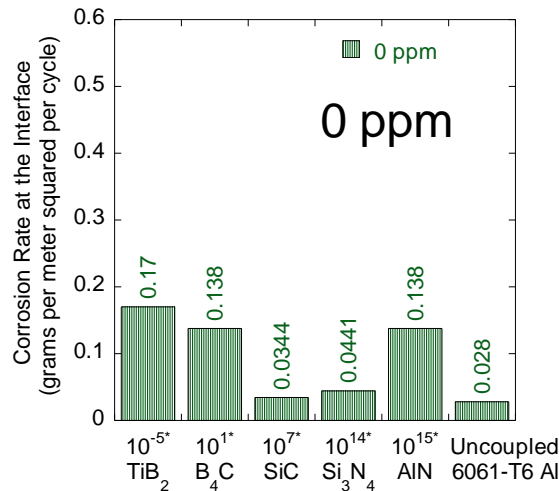
CCTC Experiment (2 cycles)

- For the 2-cycle CCTC experiment, the corrosion in the interface area of the 6061-T6 Al coupons was negligible when coupled to SiC, AlN, or Si₃N₄; whereas, corrosion had already initiated when coupled to B₄C.
- If the ceramics are insulators, accelerated corrosion at the interface is governed primarily by crevice corrosion, which requires the development of pH gradients in the crevice regions.
 - The 2-cycle experiment was likely too short for pH gradients to develop.
- In contrast, if the ceramics are conductive, galvanic corrosion can progress immediately.
 - Galvanic corrosion between the TiB₂ and the B₄C coupons does not have an “incubation” period as interface corrosion rates were high after only 2 cycles.

Results and Discussion

CCTC Experiment (24 cycles)

Various Chloride Concentrations



*Electrical resistivity of ceramics (Ω -cm)

Results and Discussion

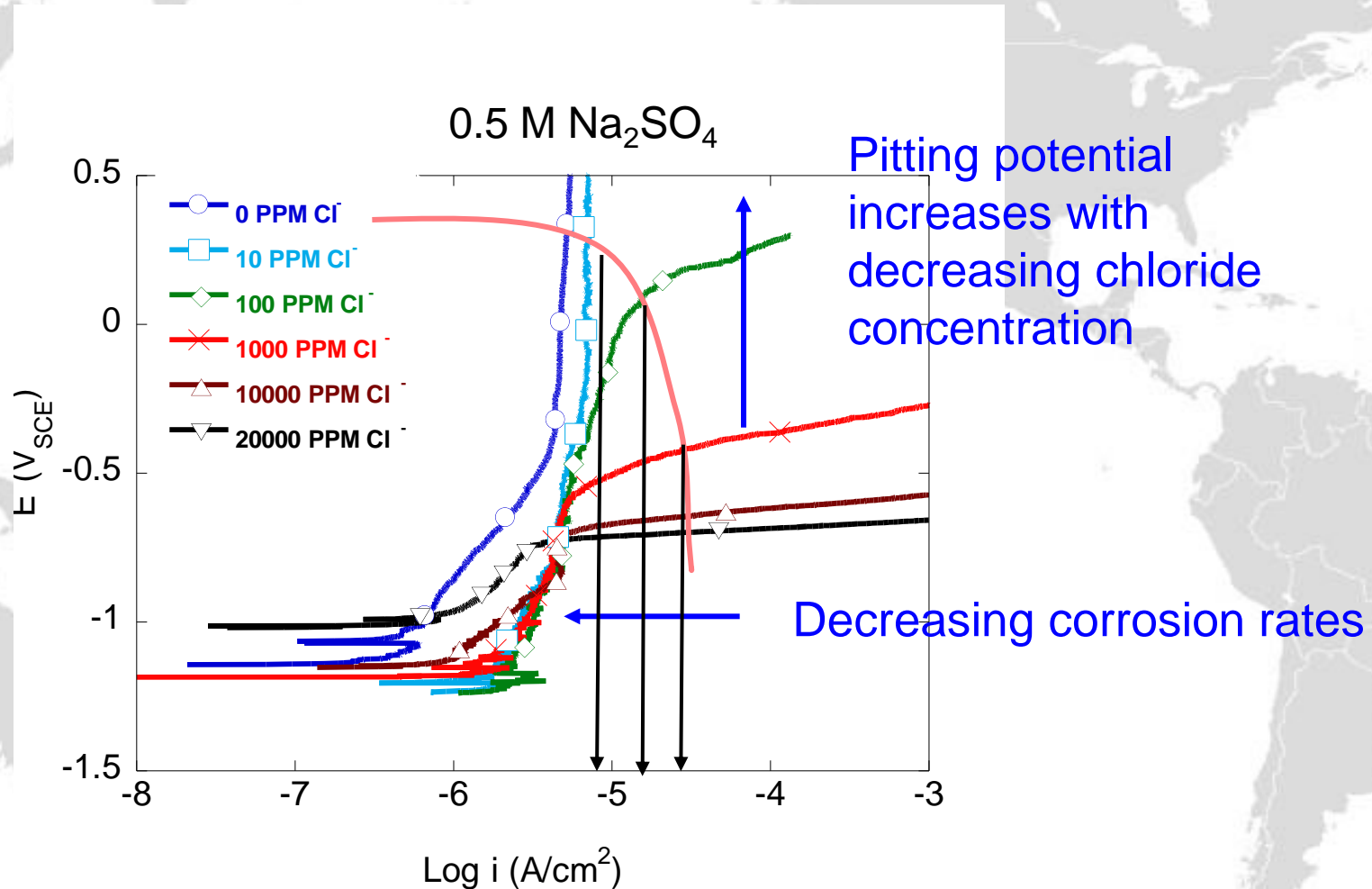
CCTC Experiment (24 cycles)

Various Chloride Concentrations

- Corrosion was observed at the interfacial region of the 6061-T6 Al coupons for both the galvanic and non-galvanic couples for the 24-cycle test.
- The 24-cycle CCTC results for aggressive chloride solution treatments (i.e., 1000, and 6000 ppm Cl) did not represent the outdoor corrosion trends and were comparable to results from the 90-day humidity chamber exposure with aggressive chloride treatments (i.e., 3.15 wt% NaCl, ASTM seawater, real seawater)
- The correlation between the outdoor experiments and CCTC experiments improved for the less aggressive chloride solution treatments (i.e., 10 and 100 ppm chloride). Chloride levels in rain water have been measured to be approximately 10 – 20 ppm.

Results and Discussion

Polarization Experiments



- Corrosivity decreases with decreasing chloride concentrations.

Conclusions

- The chloride treatments were too aggressive in the accelerated corrosion tests and did not produce corrosion trends observed at the field sites.
- Low-concentration chloride solutions may better simulate rain and; hence, the corrosion of the specimens in the field.
 - Even at marine sites, rain which is low in chlorides (approx. 10 ppm) regularly cleanses specimens of deposited aerosol chlorides.
- In the absence of chlorides, corrosion may be driven more by pH gradients that developed around the crevice; whereas, in strong chloride environments, corrosion may be driven more by pitting.
 - Hence, optimal chloride concentration in the corrosive medium may be the key to simulating outdoor corrosion tests.
- The duration of accelerated corrosion tests should be carefully selected so that corrosion mechanism (galvanic or/and crevice corrosion) that operate in the accelerated tests can better represent field conditions.

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Thank You



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